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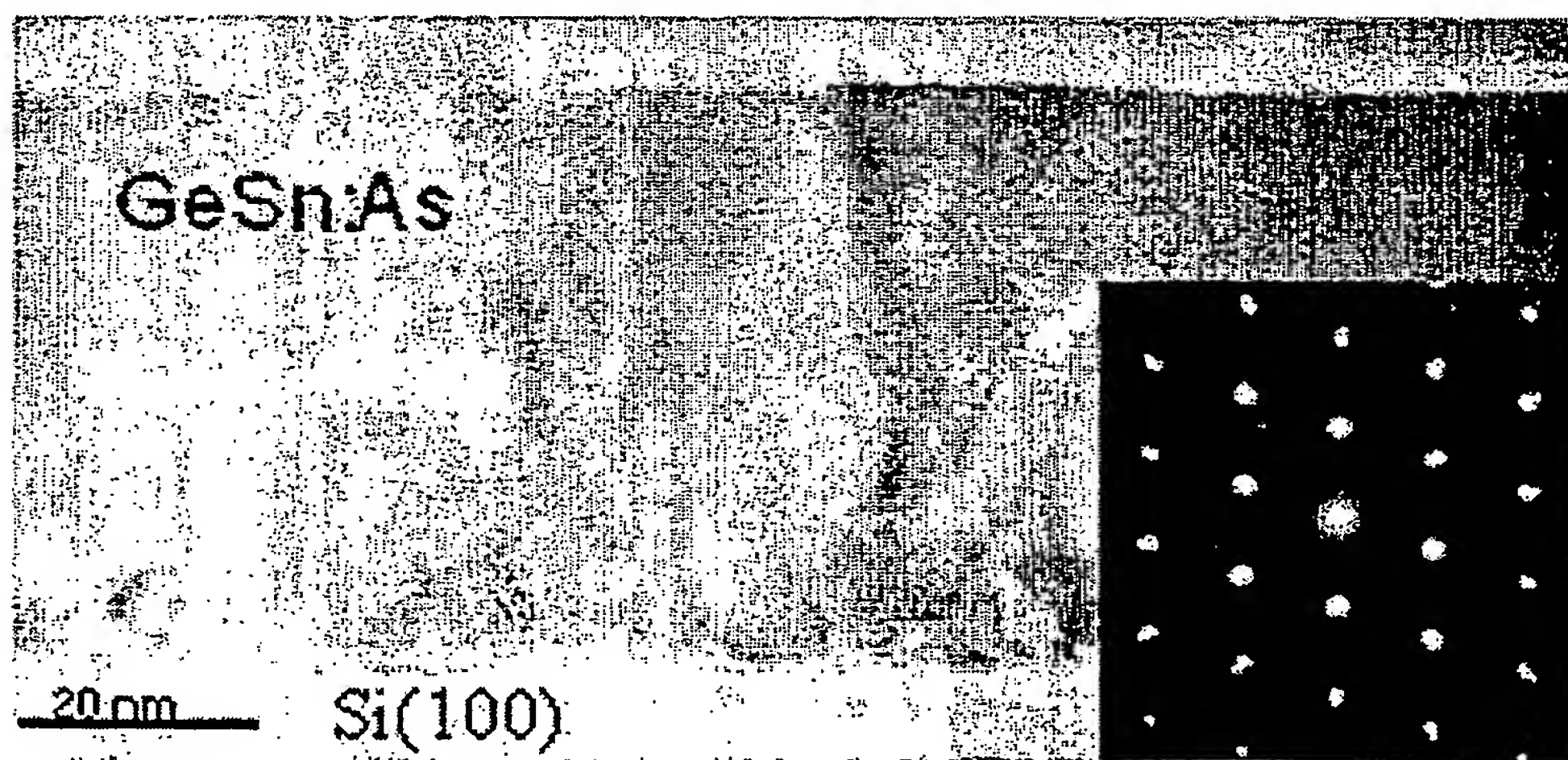
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## Declarations under Rule 4.17:

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[Continued on next page]

(54) Title: METHOD FOR PREPARING  $\text{Ge}_{1-x-y}\text{Sn}_x\text{E}_y$  (E=P, As, Sb) SEMICONDUCTORS AND RELATED Si-Ge-Sn-E AND Si-Ge-E ANALOGS



(57) Abstract: A process for is provided for synthesizing a compound having the formula  $\text{E}(\text{GeH}_3)_3$  wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P).  $\text{GeH}_3\text{Br}$  and  $[\text{CH}_3]_3\text{Si}_3\text{E}$  are combined under conditions whereby  $\text{E}(\text{GeH}_3)_3$  is obtained. The  $\text{E}(\text{GeH}_3)_3$  is purified by trap-to-trap fractionation. Yields from about 70% to about 76% can be obtained. The  $\text{E}(\text{GeH}_3)_3$  can be used as a gaseous precursor for doping a region of a semiconductor material comprising Ge, SnGe, SiGe and SiGeSn in a chemical vapor deposition reaction chamber.



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**Method for Preparing  $\text{Ge}_{1-x-y}\text{Sn}_x\text{E}_y$  (E=P, As, Sb) Semiconductors and  
Related Si-Ge-Sn-E and Si-Ge-E Analogs**

RELATED APPLICATION DATA

[0001] This application is based on and claims the benefit of U.S. Provisional Patent Application No. 60/478,480 filed on June 13, 2003, the disclosure of which is incorporated herein by this reference.

STATEMENT OF GOVERNMENT FUNDING

[0002] The United States Government provided financial assistance for this project through the National Science Foundation under Grant No. DMR 0221993 and through the Army Research Office Grant No. DAA 19-00-0-0471. Therefore, the United States Government may own certain rights to this invention.

BACKGROUND

[0003] This invention relates generally to semiconductor materials and, more particularly, to doping and superdoping *in situ* a broad family of Si-based semiconductors such as Ge, SnGe, SiGe, and SiGeSn with As, P, and Sb (Group V element).

[0004] It has been known for many years—on theoretical grounds—that the SnGe alloy system and the SiGeSn alloy system should have properties that would be very beneficial in microelectronic and optoelectronic devices. This has stimulated intense experimental efforts to grow such compounds. For many years the resulting material quality has been incompatible with device applications. Recently, however, we successfully synthesized device-quality SnGe alloys directly on Si substrates. See M. Bauer, J. Taraci, J. Tolle A.V.G Chizmeshya, S. Zollner, J. Menendez, D. J. Smith and J. Kouvetakis, *Appl. Phys. Lett* 81, 2992 (2002); M. R. Bauer, J. Kouvetakis, D.J. Smith and J. Menendez, *Solid State Commun* . 127, 355 (2003); M.R. Bauer, P. Crozier, A.V.G Chizmeshya and J. D. Smith and J. Kouvetakis *Appl. Phys. Lett.* 83, 3489 (2003), which are incorporated herein by this reference.

[0005] In order to fabricate devices using these materials, however, it is necessary to dope thin films of the materials with donor and acceptor elements, such as B, P, As and Sb. Previously known methods for doping Si-based semiconductors with As or P have significant limitations. Typically n-doping is performed using a molecular source approach or by ion implantation using solid sources of the dopant elements. Ion implantation has advantages such as relatively low processing temperatures and the short processing times.

However, it also has some major disadvantages, such as significant substrate damage and composition gradients across the film. For the thermodynamically unstable Sn-Ge lattice the re-growth temperatures, that are required to repair the implantation damage of the crystal, may exceed the temperature stability range of the film, resulting in phase segregation and precipitation of Sn. In addition, with ion implantation there are limits as to how much dopant can be introduced into the structure. Ion implantation methods and conventional CVD of the well known  $\text{PH}_3$  and  $\text{AsH}_3$  analogs require severe and often hostile processing conditions and are expected to be incompatible with the properties and stability range of the relatively fragile Ge-Sn lattice. In addition  $\text{PH}_3$  and  $\text{AsH}_3$  are highly toxic and in fact can be lethal in relatively small doses.

[0006] There is a need, therefore, for a method of incorporating appropriate concentrations of activated atoms into the lattice of the Ge-Sn system and in  $\text{Ge}_{1-x-y}\text{Sn}_x\text{E}_y$  ( $\text{E}=\text{P}, \text{As}, \text{Sb}$ ) semiconductors and related Si-Ge-Sn-E and Si-Ge-E analogs. It is an object of the present invention to provide such a method.

[0007] It is another object of the present invention to such a method that is practical to implement.

[0008] Additional objects and advantages of the invention will be set forth in the description that follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by the instrumentalities and combinations pointed out herein.

### SUMMARY OF THE INVENTION

[0009] To achieve the foregoing objects, and in accordance with the purposes of the invention as embodied and broadly described in this document, we provide a novel process for incorporating group V atoms such as P, As and Sb into Ge-Sn materials and other group IV semiconductors. The process includes synthesizing a compound having the formula  $\text{E}(\text{GeH}_3)_3$  wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P). According to a preferred approach,  $\text{GeH}_3\text{Br}$  with  $[(\text{CH}_3)_3\text{Si}]_3\text{E}$  are combined under conditions whereby  $\text{E}(\text{GeH}_3)_3$  is obtained. The  $\text{E}(\text{GeH}_3)_3$  is then purified by trap-to-trap fractionation.  $\text{E}(\text{GeH}_3)_3$  can be obtained with a yield from about 70% to about 76%.

[0010] According to another aspect of the invention, a method for doping a region of a semiconductor material in a chemical vapor deposition reaction chamber is described. The method includes introducing into the chamber a gaseous precursor having the



formula  $E(\text{GeH}_3)_3$ , wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P). The semiconductor material can comprise germanium (Ge), SiGeSn, SiGe or SnGe.

**[0011]** According to another aspect of the invention, a method for depositing a doped epitaxial Ge-Sn layer on a substrate in a chemical vapor deposition reaction chamber is described. The method includes introducing into the chamber a gaseous precursor comprising  $\text{SnD}_4$  mixed in  $\text{H}_2$  under conditions whereby the epitaxial Ge-Sn layer is formed on the substrate, including a silicon substrate, and introducing into the chamber a gaseous precursor having the formula  $E(\text{GeH}_3)_3$ , wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P). The gaseous precursor is introduced at a temperature in a range of about 250°C to about 350°C.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0012]** The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate the presently preferred methods and embodiments of the invention. Together with the general description given above and the detailed description of the preferred methods and embodiments given below, they serve to explain the principles of the invention.

**[0013]** FIG. 1 shows a typical gas-phase FTIR spectrum of trigermylarsine,  $(\text{H}_3\text{Ge})_3\text{As}$  showing sharp absorption bands at 2077 (Ge-H stretching), 873, 829, 785 (Ge-H deformation), 530 and 487  $\text{cm}^{-1}$  (Ge-H rocking).

**[0014]** FIG. 2 shows the PIXE spectrum of a Ge-Sn:As film grown according to the present invention.

**[0015]** FIG. 3 is a low energy SIMS profile for Ge-Sn:As (3 at.% As concentration) grown according to the present invention.

**[0016]** FIG. 4 shows aligned and random RBS spectra represented by the low and high intensity traces, respectively, of a 120 nm  $\text{Ge}_{0.97}\text{Sn}_{0.03}$  film doped with As grown on Si according to the method of the present invention.

**[0017]** FIG. 5 is a low energy SIMS profile of a  $\text{Sn}_{0.03}\text{Ge}_{0.97}$  sample doped with As according to the present invention.

**[0018]** FIG. 6 is a cross sectional view of a layer of GeSn;As/Si(100) showing a highly uniform film thickness and smooth and continuous surface morphology.

[0019] FIG. 7 is a magnified view of the GeSn:As/Si(100) heterostructure grown according to the invention, showing that most of the defects are concentrated near the film/substrate interface while the upper portion of the layer remains relatively defect free. The inset shows an electron diffraction pattern indicating a highly aligned and epitaxial GeSn:As layer on Si.

[0020] FIG. 7 is a high resolution image of the film/substrate interface of a  $\text{Ge}_{0.97}\text{Sn}_{0.03}\text{:As}$  film grown on Si (100). The image is in the (110) projection and shows high quality heteroepitaxial character.

[0021] FIG. 8 is an atomic force microscope image of the a  $\text{Ge}_{0.97}\text{Sn}_{0.03}\text{:As}$  film grown on Si (100) according to the present invention.

### DESCRIPTION

[0022] In this specification, we describe new synthesis strategies, based on novel molecular hydride sources, to incorporate Group V atoms such as P, As and Sb into the diamond lattice of Group IV semiconductor materials, including the Ge and Si-Ge and SiGeSn systems. These sources are the trigermylphosphine  $\text{P}(\text{GeH}_3)_3$ , trigermylarsine  $\text{As}(\text{GeH}_3)_3$ , and trigermylstibine  $\text{Sb}(\text{GeH}_3)_3$  family of compounds. These molecular precursors are stable and volatile at room temperature and possess the necessary reactivity to dissociate completely at growth conditions for Ge, SiGe, SnGe or SiGeSn systems, via elimination of benign and stable byproducts that do not contaminate the film. The byproduct is the  $\text{H}_2$  molecule, indicating that the precursors must be carbon-free inorganic hydrides that incorporate the desired elements P, As and Sb within a Ge coordination environment. The reactions of these molecules with appropriate concentrations of  $\text{SnD}_4$  and/or  $(\text{GeH}_3)_2$  will generate Ge-Sn compositions doped with the desired levels of a group V element.

[0023] According to one aspect of our invention, the  $\text{As}(\text{GeH}_3)_3$ ,  $\text{Sb}(\text{GeH}_3)_3$ , and  $\text{P}(\text{GeH}_3)_3$  hydride precursors are prepared using a novel high-yield method. These precursors are then used in a novel doping method that involves *in situ* incorporation of the dopant atoms into the Ge, SiGe, SnGe or SiGeSn system. The hydride compounds are co-deposited with appropriate Si/Ge/Sn sources to form Sn-Ge or Si-Ge-Sn doped with the appropriate carrier type. In the case of As, we have succeeded in increasing the free carrier concentration by making and using precursors with direct Ge-As bonds, such as  $\text{As}(\text{GeH}_3)_3$ . This unique species is an ideal molecular source for low temperature, low cost, high efficiency doping applications that are conducted via simple, single-step processes. The compound is carbon-free inorganic hydride and is designed to furnish a basic structural unit

comprised of the dopant atom surrounded by three Ge atoms. This arrangement produces homogeneous, substitution of dopant atoms at high concentrations without clustering or segregation.

**[0024]** The  $P(GeH_3)_3$ ,  $As(GeH_3)_3$ , and  $Sb(GeH_3)_3$  precursors can be used to dope functional materials such as Ge, SiGe, SnGe or SiGeSn at levels that cannot be achieved by conventional methods. We can increase the free carrier concentration by using these precursors with direct Ge-P, Ge-As, and Ge-Sb bonds and atomic arrangements that are structurally compatible with the Ge-Sn lattice. Previous reports provide only preliminary results of the synthesis and some basic physical properties of these  $P(GeH_3)_3$ ,  $As(GeH_3)_3$ , and  $Sb(GeH_3)_3$  compounds. See S. Cradock, E. A. V. Ebsorth, G. Davidson, L. A. Woodard, *J. Chem. Soc. A*, 8, 1229, (1967); D. W. H. Rankin, A. G. E. Robiet, G. M. Sheldrick, S. Beagley, T. G. Hewit, *J. Inorg. Nucl. Chem.*, 31, 2351, (1969); E. A. V. Ebsworth, D. J. Hutchison, J. Douglas, D. W. H. Rankin, *J. Chem. Res., Synop*, 12, 393, (1980); E. A. V. Ebsworth, D. W. H. Rankin, G. M. Sheldrick, *J. Chem. Soc. A*, 11, 2828, (1968). D. E. Wingelet, A. D. Norman, *Phosphorus Sulfur*, 39, 123, (1988). These previously-described procedures, however, provide low yields and in certain cases only traces of the desired product are produced. In addition these procedures are exceedingly difficult and involve steps that can be potentially dangerous especially for the scaling up phase of the work to produce industrial-scale quantities of the desired compound. Our work demonstrates new and practical methods to prepare, isolate, purify and handle these molecules in sufficient quantities to make them useful as chemical reagents as well as CVD gas sources for semiconductor applications.

#### **Preparation of $(GeH_3)_3P$ , $(GeH_3)_3As$ , and $(GeH_3)_3Sb$ for Dopant Applications**

**[0025]** Conventional n-doping of semiconductor materials with P or As atoms is performed by use of molecular  $PH_3$  and  $AsH_3$  (the  $SbH_3$  analog is unstable) or by ion implantation using solid sources of the elements. As discussed above, ion implantation causes significant substrate damage and composition gradients across the film. For the thermodynamically unstable Sn-Ge lattice, the re-growth temperatures that will be needed to repair the implantation damage of the Sn-Ge crystal may exceed the temperature stability range of the film, resulting in phase segregation and precipitation of Sn. Therefore, for doping of the Sn-Ge lattice it is desirable to use a low-temperature molecular source approach since the introduction of the dopant takes place in situ during film growth and as host Ge-Sn the lattice is generated.

[0026] Using a typical growth process conducted by either gas-source molecular beam epitaxy (GS-MBE) or chemical vapor deposition (CVD), we chose to co-deposit a compound with the general formula  $E(\text{GeH}_3)_3$  ( $E = \text{P, As, or Sb}$ ) along with the host Ge-Sn material. We determined that this growth reaction would eliminate hydrogen and generate in situ the  $\text{Ge}_3\text{E}$  molecular core, which contains the dopant atom E surrounded by three Ge atoms. This arrangement represents a simple compositional and structural building block of the host lattice. Using the  $\text{Ge}_3\text{E}$  core as the building block would also completely exclude formation of undesirable E-E bonding arrangements that may lead to clustering or segregation of the E dopant species. Thus we believed this new approach would be most likely to yield a highly homogeneous random distribution of the dopant at distinct atomic sites throughout the film. Furthermore, the doping levels could be precisely controlled by careful adjustment of the flux rate of the precursor during the course of the layer growth. An important benefit of  $\text{As}(\text{GeH}_3)_3$  [or  $\text{P}(\text{GeH}_3)_3$ ] is its higher reactivity compared to  $\text{AsH}_3$ , which allows lower deposition temperatures than those employed in conventional CVD doping processes utilizing  $\text{AsH}_3$  and related hydrides of phosphorus.

[0027] Numerous publications in the literature deal with synthesis, properties and reactions of the compounds  $(\text{Me}_3\text{Si})_3\text{E}$ ,  $(\text{Me}_3\text{Ge})_3\text{E}$ ,  $(\text{Me}_3\text{Sn})_3\text{E}$ , and  $(\text{Me}_3\text{Pb})_3\text{E}$  ( $E = \text{P, As or Sb}$ ), which are the organometallic analogs of the desired precursors. See G. A. Forsyth, D. W. H. Rankin, H. E. Robertson, *J. Mol. Struct.* **239**, 209, (1990); H. Schumann, H. J. Kroth, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **32B**, 523, (1977); G. Becker, H. Freudenblum, O. Mundt, M. Reti, M. Sachs, *Synthetic Methods of Organometallic and Inorganic Chemistry*, **3**, 193, (1996); S. Schulz, M. Nieger, *J. of Organomet. Chem.* **570**, 275, (1998); H. Schumann, U. Frank, W. W. Du Mont, F. Marschner, *J. Organomet. Chem.* **222**, 217, (1981); M. Ates, H. J. Breunig, M. Denker, *Phosphorus, Sulfur Silicon Relate. Elem.* **102**, 287, (1995); H. Schumann, A. Roth, O. Stelzer, M. Schmidt, *Inorg. Nucl. Chem. Lett.* **2**, 311, (1966). These materials have been widely utilized as common reagents in classical metathesis reactions to produce numerous molecular systems that incorporate the  $(\text{Me}_3\text{Si})_2\text{E}$ ,  $(\text{Me}_3\text{Ge})_2\text{E}$ , and  $(\text{Me}_3\text{Sn})_2\text{E}$  ligands. However, there has been relatively little activity associated with the corresponding hydrides (which are completely free of strong C-H bonds that introduce carbon contaminants in the films) despite their potential importance as precursors for deposition of novel microelectronic and optoelectronic materials.

[0028] The  $(\text{SiH}_3)_3\text{E}$  family of molecules has been synthesized and their properties have been investigated. See G. Davidson, L. A. Woodward, E. A. V. Ebsworth, G. M. Sheldrick, *Spectrochim. Acta, Part A*, **23**, 2609, (1967); B. Beagley, A. G. Robiette, G.



M. Sheldrick, *Chem. Commun*, 12, 601, (1967); A. Blake, E. A. V. Ebsworth, S. G. D. Henderson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*, C47, 489, (1991); H. Siebert, J. Eints, *J. Mol. Struct.* 4, 23, (1969); D. C. McKean, *Spectrochim. Acta, Part A*, 24, 1253, (1968); J. E. Drake, J. Simpson, *J. Chem. Soc. A* 5 1039, (1968). The high reactivity of the Si-H bonds and the absence of carbon from the molecular architecture indicated to us that these compounds could be ideal sources for low temperature depositions of semiconductors doped with P and As. The known methods for synthesizing these compounds, however, are complex and require use and manipulation of highly toxic, explosive and pyrophoric reagents such as  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{KPH}_2$ . In addition, the reported reaction yields are too low to even be considered useful for routine laboratory applications. Thus, we determined that the synthetic routes of these compounds could not be viable for large scale industrial use.

[0029] On the other hand, there have been very few reports concerning the germanium analogs  $(\text{GeH}_3)_3\text{E}$ . See S. Cradock, E. A. V. Ebsorth, G. Davidson, L. A. Woodard, *J. Chem. Soc. A*, 8, 1229, (1967); D. W. H. Rankin, A. G. E. Robiet, G. M. Sheldrick, 5 Beagley, T. G. Hewit, *J. Inorg. Nucl. Chem.*, 31, 2351, (1969); E. A. V. Ebsworth, D. J. Hutchison, J. Douglas, D. W. H. Rankin, *J. Chem. Res., Synop*, 12, 393, (1980); E. A. V. Ebsworth, D. W. H. Rankin, G. M. Sheldrick, *J. Chem. Soc. A*, 11, 2828, (1968); D. E. Wingelet, A. D. Norman, *Phosphorus Sulfur*, 39, 123, (1988). These papers describe initial preparation methods and preliminary identifications of such compounds. However, the yields obtained and the experimental synthetic procedures described are not viable for industrial or laboratory applications. Moreover, we found no report describing the tin  $(\text{SnH}_3)_3\text{Sn}$  and lead  $(\text{PbH}_3)_3\text{Pb}$  species. We decided to investigate  $(\text{GeH}_3)_3\text{P}$ ,  $(\text{GeH}_3)_3\text{As}$ ,  $(\text{GeH}_3)_3\text{Sb}$  as desirable compounds for the synthesis of  $\text{Ge}_{1-x-y}\text{Sn}_x\text{P}(\text{As,Sb})_y$  systems.

[0030]  $(\text{GeH}_3)_3\text{P}$  has been previously obtained by treating a small excess of  $\text{GeH}_3\text{Br}$  with  $(\text{SiH}_3)_3\text{P}$  as illustrated by the equation:



No yield was reported and the product was characterized by hydrogen analysis,  $^1\text{H}$  and  $^{31}\text{P}$  NMR, IR and mass spectroscopy.  $(\text{GeH}_3)_3\text{P}$  was described as a colorless liquid with a melting point of  $-83.8^\circ\text{C}$  and a vapor pressure of 1 mmHg at  $0^\circ\text{C}$ . See S. Cradock, E. A. V. Ebsorth, G. Davidson, L. A. Woodard, *J. Chem. Soc. A*, 8, 1229, (1967); D. W. H. Rankin, A. G. E. Robiet, G. M. Sheldrick, 5 Beagley, T. G. Hewit, *J. Inorg. Nucl. Chem.*, 31, 2351. Before the method of our invention, the  $(\text{GeH}_3)_3\text{As}$  and  $(\text{GeH}_3)_3\text{Sb}$  compounds were prepared in low yields by the reaction of bromogermane with the corresponding silyl compounds

(which as indicated above are difficult to produce in sufficient yields to be practical reagents for routine laboratory synthesis). See E. A. V. Ebsworth, D. W. H. Rankin, G. M. Sheldrick, *J. Chem. Soc. A*, 11, 2828, (1968).  $(\text{GeH}_3)_3\text{As}$  and  $(\text{GeH}_3)_3\text{Sb}$  were identified and characterized by NMR, IR, and Raman spectroscopies. These molecules were found to decompose very slowly, over time, at room temperature to give germane and an unidentified involatile substance. Their vapor pressures were not reported but there was mention of distilling the liquids onto CsBr plates to obtain IR spectra, indicating that they are sufficiently volatile to allow significant mass transport under vacuum.

[0031]  $(\text{GeH}_3)_3\text{P}$  has also been synthesized by the redistribution reaction of silylphosphines and germylphosphines in the presence of  $\text{B}_5\text{H}_9$ , as described by Wingleth, A. D. Norman, *Phosphorus Sulfur*, 39, 123, (1988). In these reactions,  $\text{B}_5\text{H}_9$  and  $\text{GeH}_3\text{PH}_2$  were intermixed in the gas phase at room temperature and the trigermylphosphine (20% yield) was found in the reaction vessel along with  $\text{PH}_3$ ,  $\text{GeH}_4$ , and unreacted starting material.

[0032] According to a preferred method of the present invention, we provide a new, convenient and high yield method to prepare  $(\text{GeH}_3)_3\text{P}$ ,  $(\text{GeH}_3)_3\text{As}$ , and  $(\text{GeH}_3)_3\text{Sb}$ . This trigermyl family of compounds is safer and easier to handle and store than reagents such as  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{KPH}_2$ . This new method is based on the general reaction described by the equation below, and provides large concentrations of the final product (>70 %) to allow thorough characterization, purification and ultimately routine application in film growth. According to this method, the more common and relatively inexpensive trimethylsilyl derivatives  $[(\text{CH}_3)_3\text{Si}]_3\text{E}$ ,  $\{[(\text{CH}_3)_3\text{Si}]_3\text{P}, [(\text{CH}_3)_3\text{Si}]_3\text{As}, [(\text{CH}_3)_3\text{Si}]_3\text{Sb}\}$ , are used as starting materials. Straightforward, large scale syntheses of these compounds is well known to those of skill in the art. The synthesis of  $\text{E}(\text{GeH}_3)_3$  is achieved by the reaction of  $\text{GeH}_3\text{Br}$  with  $[(\text{CH}_3)_3\text{Si}]_3\text{E}$  according to the following equation:



$\text{GeH}_3\text{Br}$  is readily obtained by a single step reaction of  $\text{GeH}_4$  with  $\text{Br}_2$ . The  $(\text{GeH}_3)_3\text{E}$  products are obtained as colorless volatile liquids and are purified by trap-to-trap fractionation.

[0033] Using this method of the present invention, we have obtained yields of the  $(\text{GeH}_3)_3\text{E}$  products typically ranging from 70% to 76%. The  $^1\text{H}$  NMR and gas phase IR data of the products are consistent with the  $(\text{GeH}_3)_3\text{P}$ ,  $(\text{GeH}_3)_3\text{As}$  and  $(\text{GeH}_3)_3\text{Sb}$  molecular structures. These data conclusively reveal that we are able to synthesize and purify the desired compounds. FIG. 1 shows a typical gas-phase FTIR spectrum of trigermylarsine,

(H<sub>3</sub>Ge)<sub>3</sub>As showing sharp absorption bands at 2077 (Ge-H stretching), 873, 829, 785 (Ge-H deformation), 530 and 487 cm<sup>-1</sup> (Ge-H rocking). The <sup>1</sup>H NMR spectroscopy (not shown) consisted of a sinlet Ge-H resonsnce at 3.896 ppm. The gas-phase IR spectrum is nearly identical with that of (H<sub>3</sub>Ge)<sub>3</sub>P (which we synthesized using the same synthetic methodology) with a slight shift in absorption bands to lower wave numbers.

[0034] We have used the (GeH<sub>3</sub>)<sub>3</sub>E compounds synthesized according to the preferred process described above as dopant sources to perform a survey of growth experiments to develop new semiconductor films on Si (100) using CVD. An alternative method for generating suitable dopant sources involves the preparation of the general family of compounds EH<sub>x</sub>(GeH<sub>3</sub>)<sub>3-x</sub> where x=1,2 and E=P, As, Sb. These can be synthesized by reaction of inorganic or orhanometallic compounds of the E element with alkali germyls such as KGeH<sub>3</sub> or halogenated germanes such as BrGeH<sub>3</sub>. The products can be readily isolated and purified to give semiconductor grade reagents for in situ doping applications.

[0035] The following examples help to further explain the method described above. It will be understood, however, that the examples are illustrative of the process and materials of the invention and that the invention is not limited only to these examples.

#### CVD Depositions of As(GeH<sub>3</sub>)<sub>3</sub>

[0036] Depositions of pure trigermylarsine (As(GeH<sub>3</sub>)<sub>3</sub>) *via* ultra-high vacuum CVD (UHV-CVD) showed that the molecule decomposes on Si (100) at temperatures as low as 350°C to form thin films with approximately 30 at. % As. This indicates that the entire Ge<sub>3</sub>As molecular core is incorporated into the deposited material. Low-pressure CVD growth of As-doped Ge<sub>1-x</sub>Sn<sub>x</sub> films was also demonstrated. Arsenic concentrations up to 3 at. % were obtained. Doping level incorporations were also achieved by reactions of appropriate concentrations of As(GeH<sub>3</sub>)<sub>3</sub>.

[0037] Our initial growth experiments demonstrated that compositional control of As in Ge-Sn can be obtained by simply varying the partial pressure of the reactant gases As(GeH<sub>3</sub>)<sub>3</sub>, SnD<sub>4</sub> and Ge<sub>2</sub>H<sub>6</sub>. We characterized the sample films using RBS to determine the Ge to Sn ratio and using particle-induced X-ray emission (PIXE) to determine the As concentrations. FIG. 2 shows the PIXE spectrum of sample Ge-Sn:As films. Quantification obtained from fitting the peaks shows that the sample films contained about 3 at. % As. We used Secondary Ion Mass Spectrometry depth profile analysis (SIMS) to determine the As elemental distribution and Hall/FTIR ellipsometry measurements to determine carrier concentrations and effective masses. Initial deposition studies have shown



that As is readily incorporated into the Ge-Sn lattice. Low energy SIMS of the samples showed highly homogeneous profiles of As and the Ge and Sn constituent elements throughout the film. FIG. 3 is a low energy SIMS profile for a Ge-Sn:As (3 at% As concentration) sample. We used TEM to show that the microstructure and epitaxial character of the sample film is of good quality. X-ray diffraction showed that the sample film had an average diamond cubic lattice.

[0038] Following our initial growth experiments, we performed additional experiments using the process of our invention to grow sample  $\text{Ge}_{1-x}\text{Sn}_x$  films doped with As atoms to determine optimal growth conditions for yielding high quality layers with crystalline perfection and phase homogeneity required for many desirable device applications. For these experiments, we utilized UHV-CVD reaction of  $\text{SnD}_4$ ,  $\text{Ge}_2\text{H}_6$  and  $\text{As}(\text{GeH}_3)_3$  at  $350^\circ\text{C}$ . Concentrations of the reactants were selected to obtain the desired composition in the alloy.

[0039] FIGs. 4-9 show results of our characterization of a resulting  $\text{Ge}_{0.97}\text{Sn}_{0.03}$  film doped in situ with arsenic using the  $\text{As}(\text{GeH}_3)_3$  compound as the source of the As atoms. Again, we used Rutherford backscattering (RBS) to determine the bulk concentration of the resulting films and low energy SIMS to obtain the As elemental profile. FIG. 4 shows a typical RBS spectrum of a Ge-Sn sample doped with As. The Ge and Sn concentrations were found to be 97% and 3 at. %, respectively. The As content was determined by SIMS to be  $1.71 \times 10^{21}$  atoms/cm<sup>3</sup>. The channeling for both Ge and Sn is identical, indicating that the material is single phase and that the elements occupy substitutional sites in the same average diamond structure. FIG. 5 shows a low energy SIMS profile of a  $\text{Sn}_{0.03}\text{Ge}_{0.97}$  sample doped with As. The elemental profiles indicate that the films have a highly uniform As concentration throughout the sample. These SIMS data were used to quantify the dopant content using implanted samples of known concentration as a standard, and the As content of the  $\text{Sn}_{0.03}\text{Ge}_{0.97}$  sample was determined to be  $\sim 10^{21}$  atoms per cm<sup>3</sup>.

[0040] FIGs. 6-8 show cross sectional electron micrographs of the Ge-Sn:As sample films, which indicate single crystal quality, a high degree of epitaxial alignment and smooth surface morphology. FIG. 6 is a cross sectional view of the entire layer of a GeSn:As/Si(100) sample showing a highly uniform film thickness and smooth and continuous surface morphology. FIG. 7 is a magnified view of the GeSn:As/Si(100) heterostructure showing that most of the defects are concentrated near the film/substrate interface while the upper portion of the layer remains relatively defect free. The inset of FIG. 7 is a selected area electron diffraction pattern which shows that the epitaxial GeSn:As layer



is highly aligned on the Si substrate. FIG. 8 is a high resolution image of the interface in the (110) projection showing high quality heteroepitaxial character.

[0041] Atomic force microscopy was used to examine the surface structure and morphology of the  $\text{Ge}_{0.97}\text{Sn}_{0.03}\text{:As}$  film. FIG. 9 is an atomic force microscopy (AFM) image of such a film, showing extremely smooth surface topology with a typical RMS value of 0.7 nm.

### CONCLUSION

[0042] The above-described invention possesses numerous advantages as described herein. The invention in its broader aspects is not limited to the specific details, representative devices, and illustrative examples shown and described. Those skilled in the art will appreciate that numerous changes and modifications may be made to the preferred embodiments of the invention and that such changes and modifications may be made without departing from the spirit of the invention. It is therefore intended that the appended claims cover all such equivalent variations as fall within the true spirit and scope of the invention.

**WHAT IS CLAIMED IS:**

1. A method for synthesizing a compound having the formula  $E(\text{GeH}_3)_3$  wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P), the method comprising combining  $\text{GeH}_3\text{Br}$  with  $[(\text{CH}_3)_3\text{Si}]_3\text{E}$  under conditions whereby  $E(\text{GeH}_3)_3$  is obtained.
2. The method of claim 1 further comprising purifying the obtained  $E(\text{GeH}_3)_3$ .
3. The method of claim 1 wherein the step of purifying the obtained  $E(\text{GeH}_3)_3$  comprises trap-to-trap fractionation.
4. The method of claim 1 wherein  $E(\text{GeH}_3)_3$  is obtained with a yield from about 70% to about 76%.
5. A method for synthesizing a compound having the formula  $E(\text{GeH}_3)_3$  wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P), the method comprising combining  $\text{GeH}_3\text{Br}$  with  $[(\text{CH}_3)_3\text{Si}]_3\text{E}$  to obtain  $E(\text{GeH}_3)_3$  according to the formula:  

$$3 \text{ GeH}_3\text{Br} + [(\text{CH}_3)_3\text{Si}]_3\text{E} \rightarrow 3 (\text{CH}_3)_3\text{Si Br} + (\text{GeH}_3)_3\text{E}$$
6. The method of claim 5 further comprising purifying the obtained  $E(\text{GeH}_3)_3$ .
7. The method of claim 5 wherein the step of purifying the obtained  $E(\text{GeH}_3)_3$  comprises trap-to-trap fractionation.
8. The method of claim 5 wherein  $E(\text{GeH}_3)_3$  is obtained with a yield from about 70% to about 76%.
9. A method for doping a region of a semiconductor material in a chemical vapor deposition reaction chamber, the method comprising introducing into the chamber a gaseous precursor having the formula  $E(\text{GeH}_3)_3$ , wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P).
10. The method of claim 9 wherein the semiconductor material comprises silicon (Si).
11. The method of claim 9 wherein the semiconductor material comprises germanium (Ge).

12. The method of claim 9 wherein the semiconductor material comprises SiGeSn.
13. The method of claim 9 wherein the semiconductor material comprises SnGe.
14. A method for depositing a doped epitaxial Ge-Sn layer on a substrate in a chemical vapor deposition reaction chamber, the method comprising:
  - introducing into the chamber a gaseous precursor comprising  $\text{SnD}_4$  mixed in  $\text{H}_2$  under conditions whereby the epitaxial Ge-Sn layer is formed on the substrate; and
  - introducing into the chamber a gaseous precursor having the formula  $\text{E}(\text{GeH}_3)_3$ , wherein E is selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P).
15. The method of claim 14 wherein the gaseous precursor is introduced at a temperature in a range of about  $250^\circ\text{C}$  to about  $350^\circ\text{C}$ .
16. The method of claim 14 wherein the substrate comprises silicon.
17. The method of claim 14 wherein the silicon comprises Si(100).
18. The method of claim 14 wherein the Ge-Sn layer comprises  $\text{Sn}_x\text{Ge}_{1-x}$  and  $x$  is in a range from about .02 to about .20.
19. A method for forming a Group IV semiconductor film, the method comprising
  - forming the Group IV semiconductor by a chemical vapor deposition method, said Group IV semiconductor film being doped with impurities at a concentration ranging from about  $10^{21}$  atoms/ $\text{cm}^3$  to about several percent, the impurities being selected from the group consisting of arsenic (As), phosphorous (P) and antimony (Sb).
20. A method for forming a Group IV semiconductor film, the method comprising:
  - forming the Group IV semiconductor film by a chemical vapor deposition method; and
  - while forming the Group IV semiconductor film, doping the film with impurities at a concentration ranging from about  $10^{21}$  atoms/ $\text{cm}^3$  to about 3 at. %, the impurities being selected from the group consisting of arsenic (As), antimony (Sb) and phosphorus (P)

21. The method for forming a Group IV semiconductor film according to claim 20, wherein arsenic (As), antimony (Sb) and phosphorus (P) are added to the Group IV semiconductor film by diffusion methods.
22. The method for forming a Group IV semiconductor film according to claim 20, wherein said doping step comprises introducing the As, P, or Sb impurities into a reaction chamber as hydride compounds, together with at least  $\text{SnD}_4$ ,  $\text{GeH}_4$ ,  $\text{Ge}_2\text{H}_6$ .
23. A method of preparing  $(\text{E})\text{H}_x(\text{GeH}_3)_{3-x}$ , where  $x=1$  or  $2$  and E is selected from the group consisting of P, As, Sb, the method comprising reacting inorganic or organometallic compounds of the E element with an alkali germyl or a halogenated germane.
24. The method of preparing  $(\text{E})\text{H}_x(\text{GeH}_3)_{3-x}$  according to claim 23 wherein the alkali germyl comprises  $\text{KGeH}_3$ .
25. The method of preparing  $(\text{E})\text{H}_x(\text{GeH}_3)_{3-x}$  according to claim 23 wherein the halogenated germane comprises  $\text{BrGeH}_3$ .



1 / 5

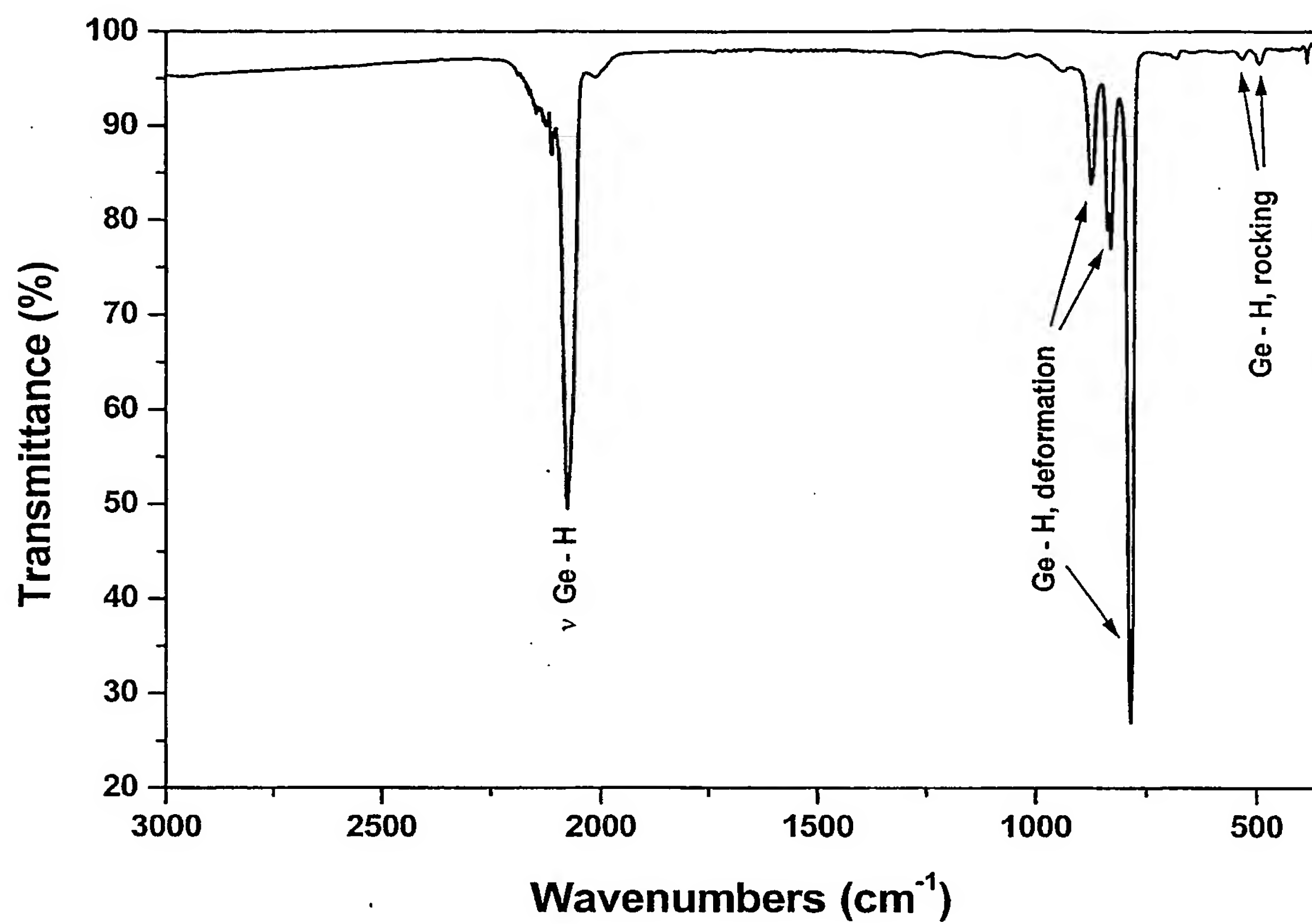


FIG. 1

2 / 5

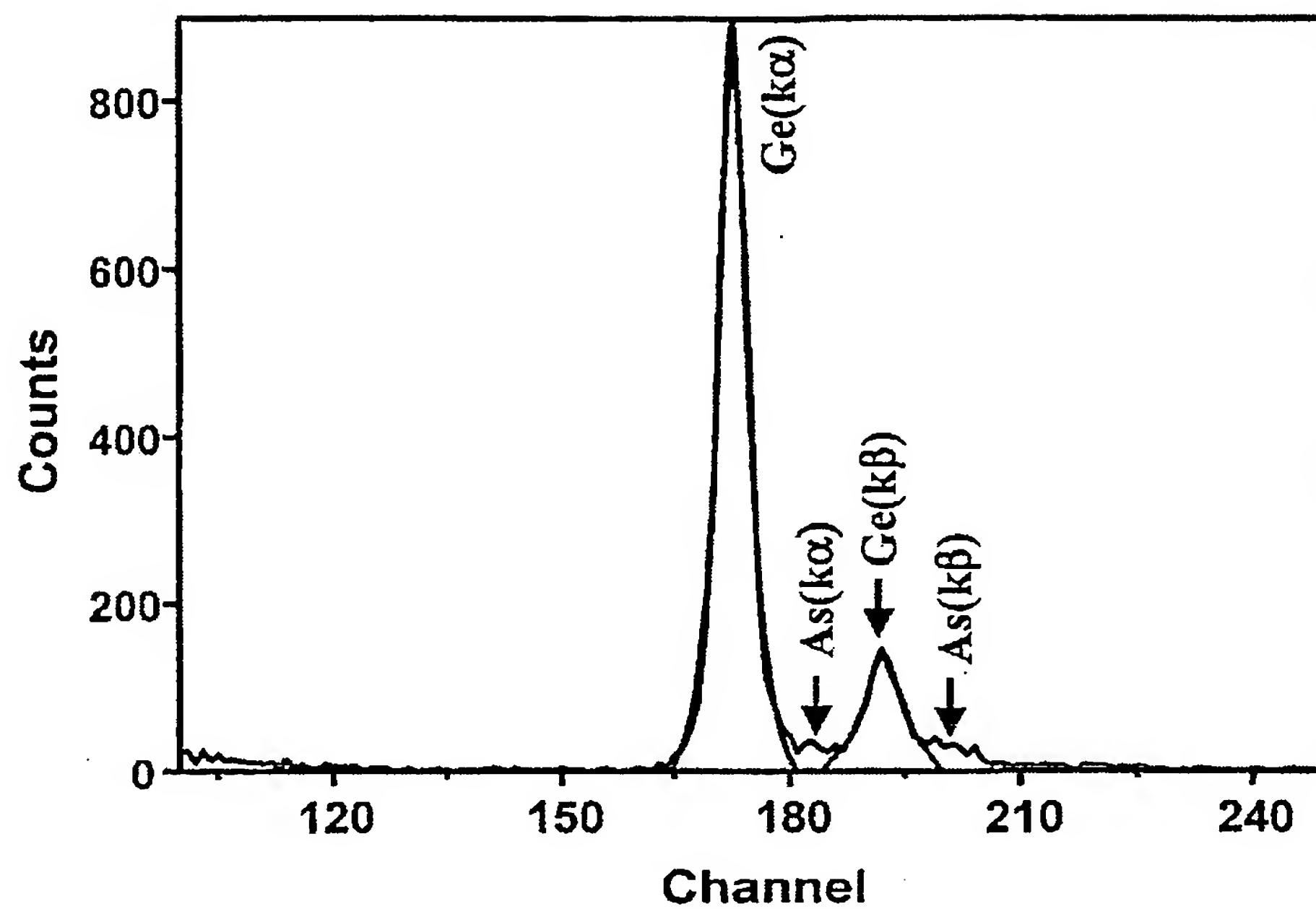


FIG. 2

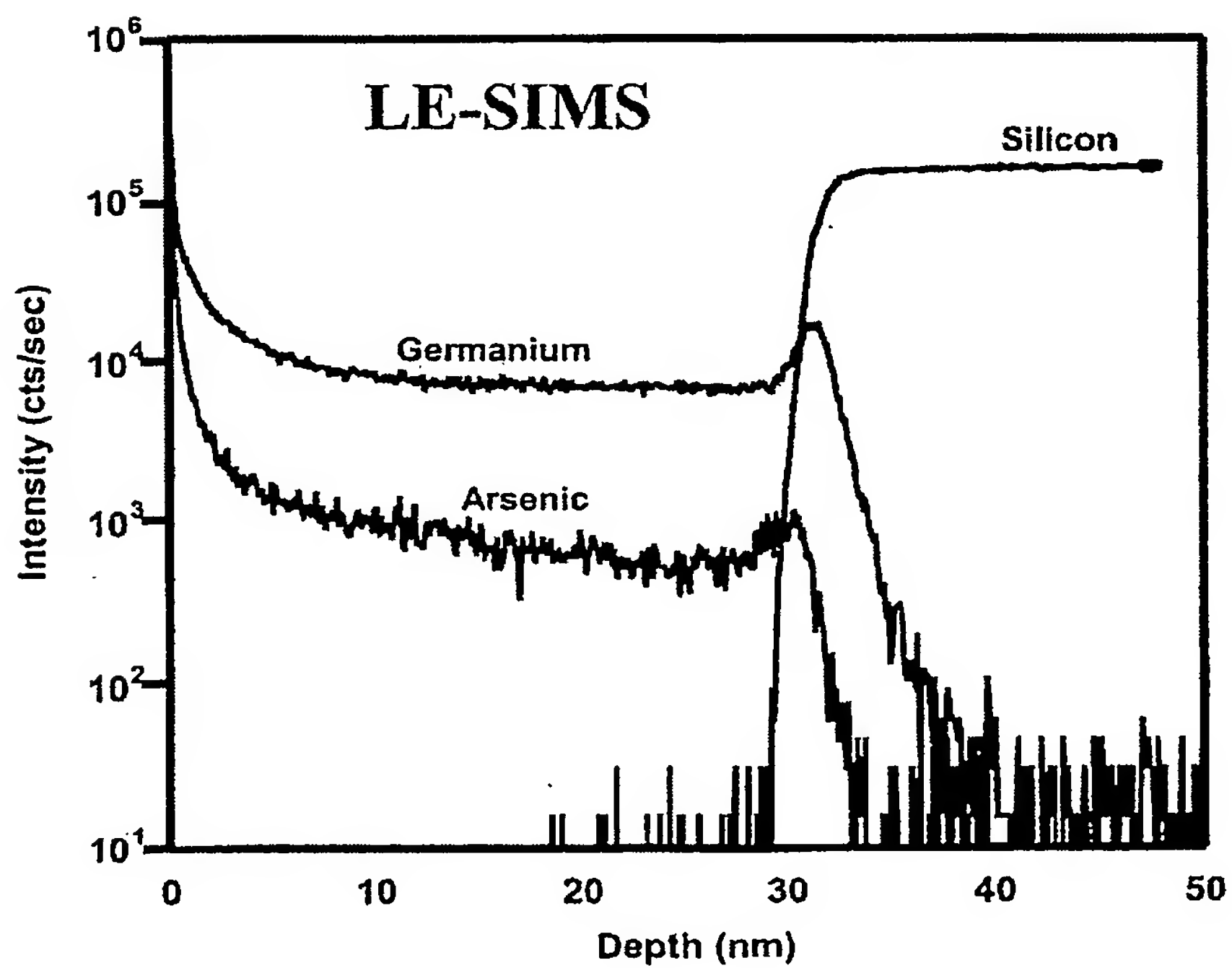


FIG. 3

3 / 5

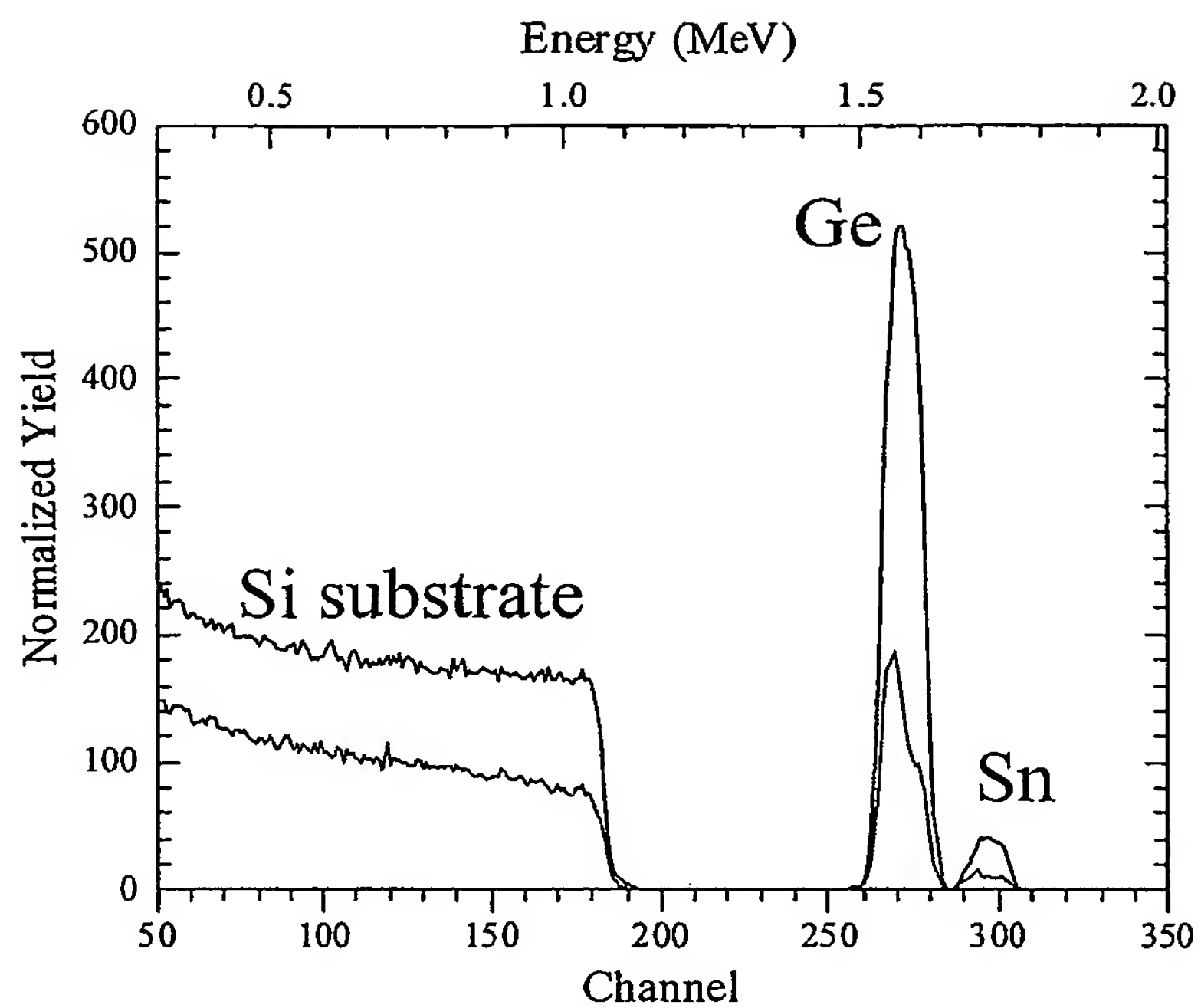


FIG. 4

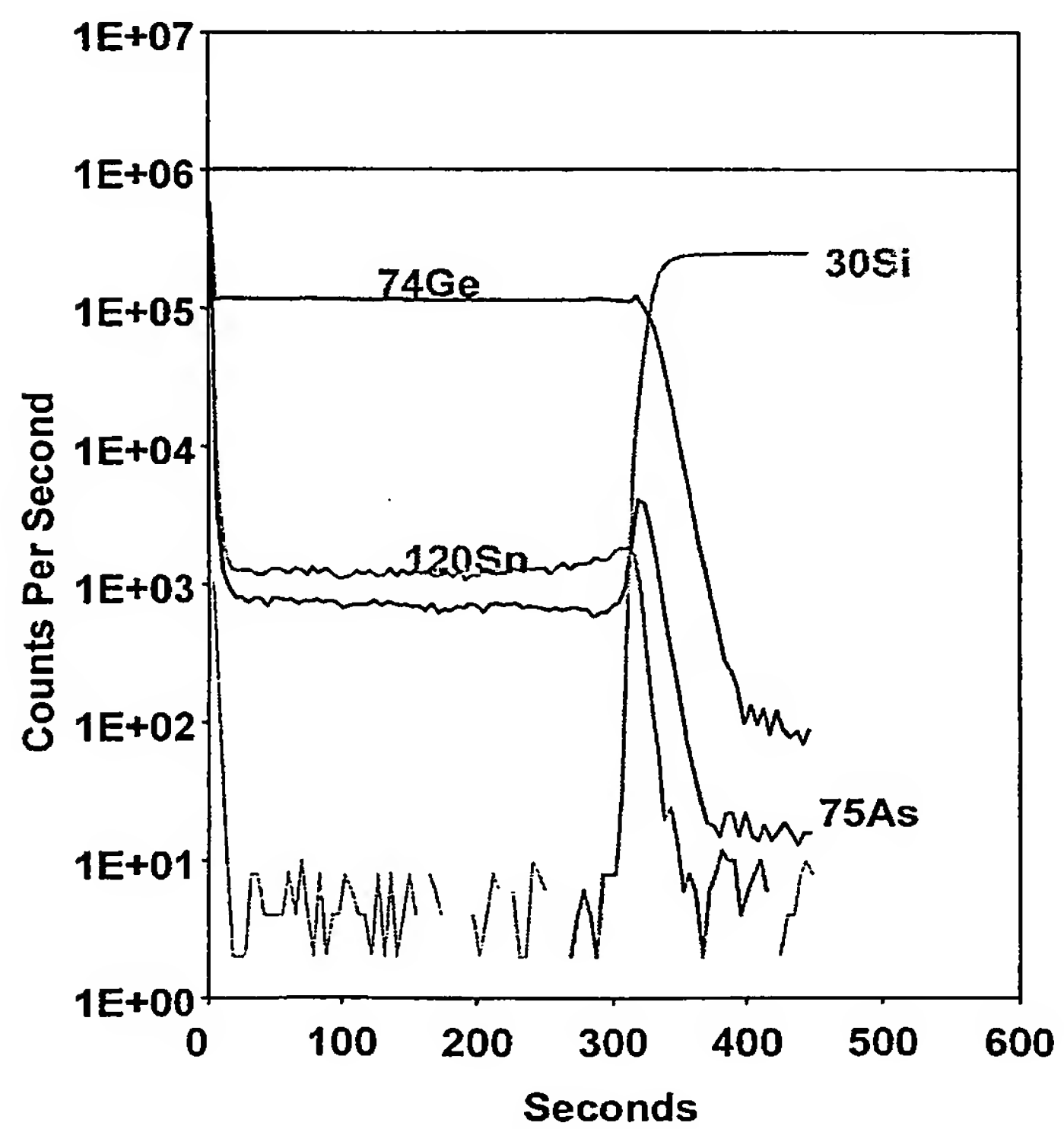


FIG. 5



FIG. 6

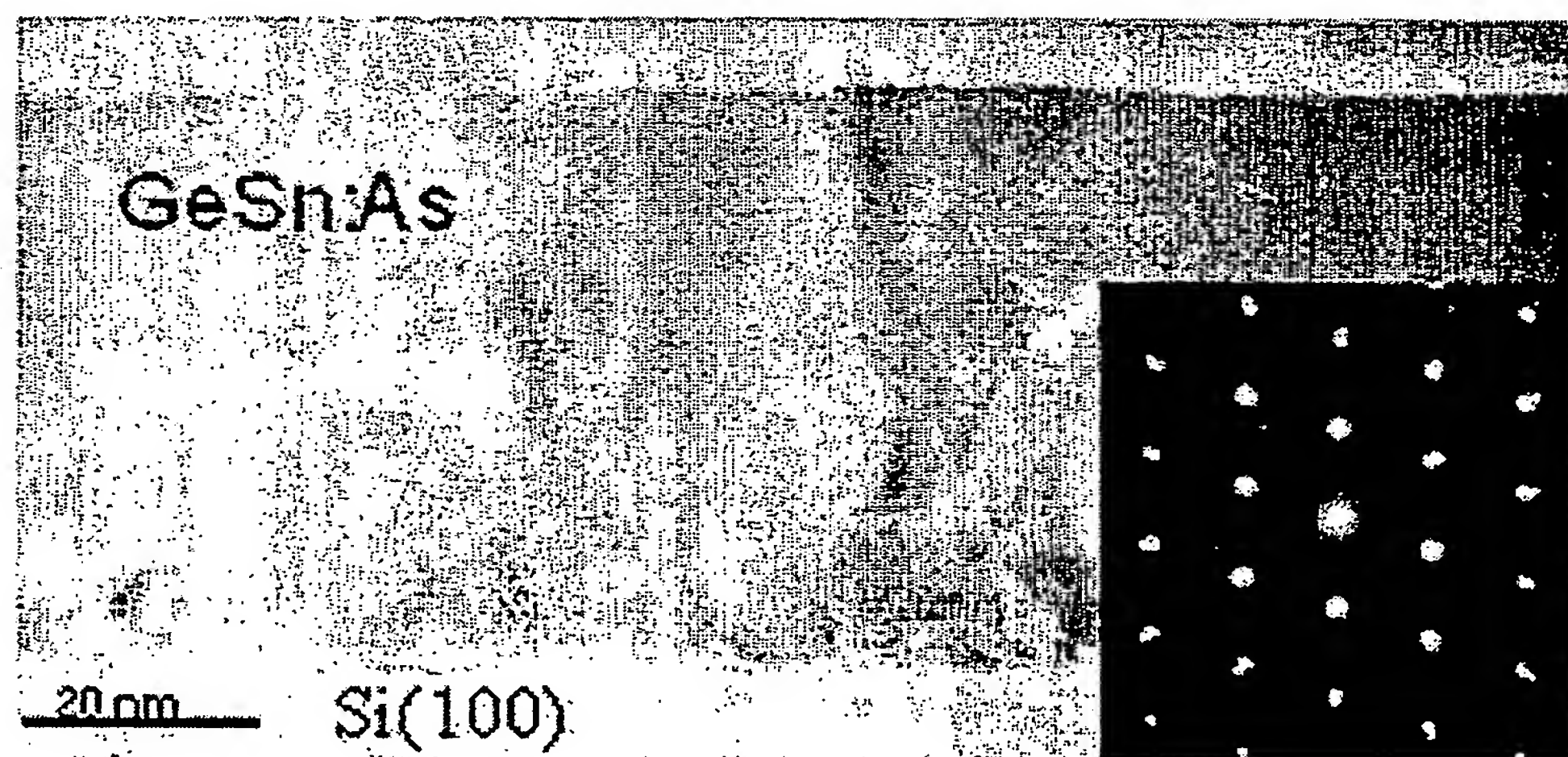


FIG. 7



5 / 5

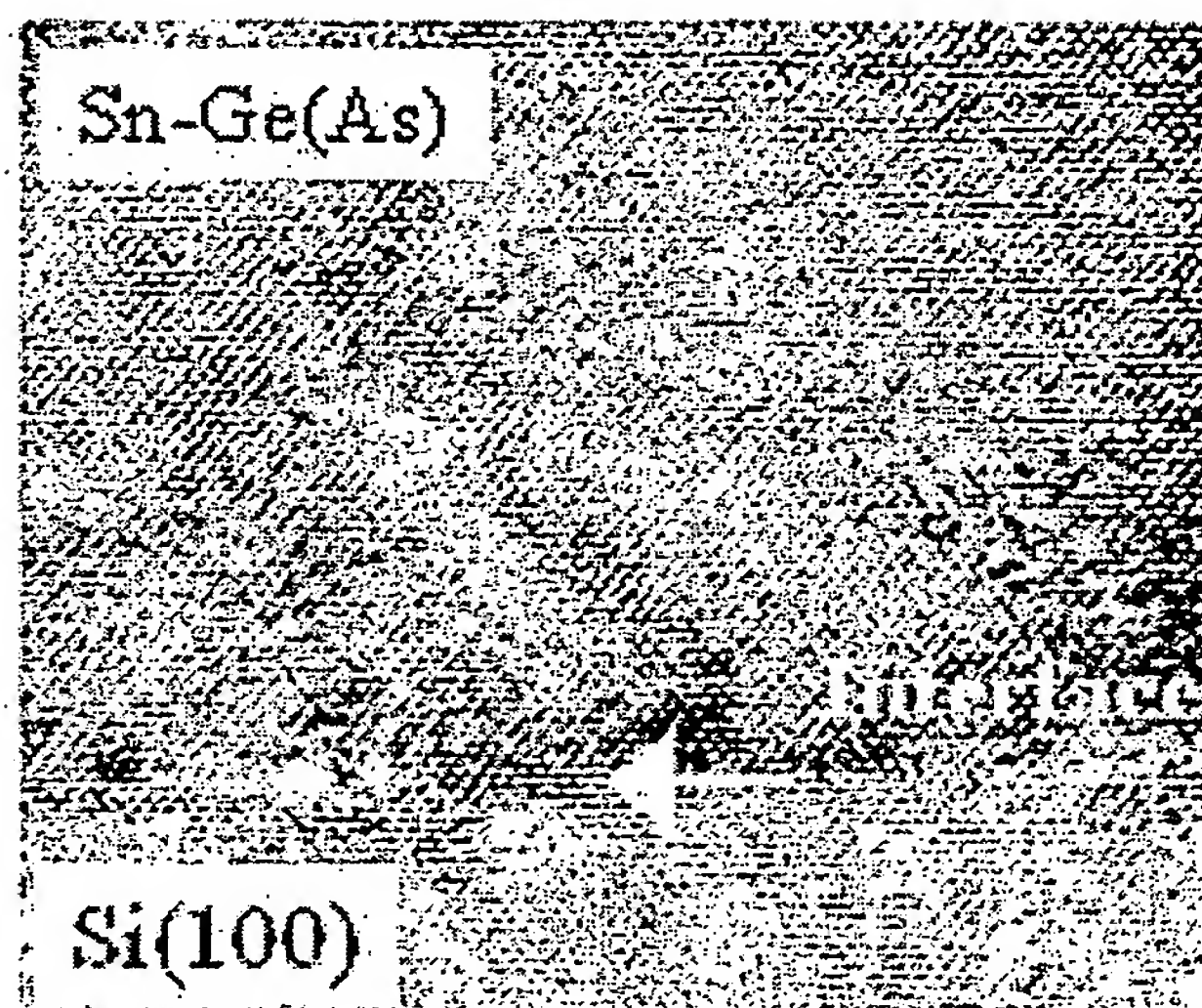


FIG. 8

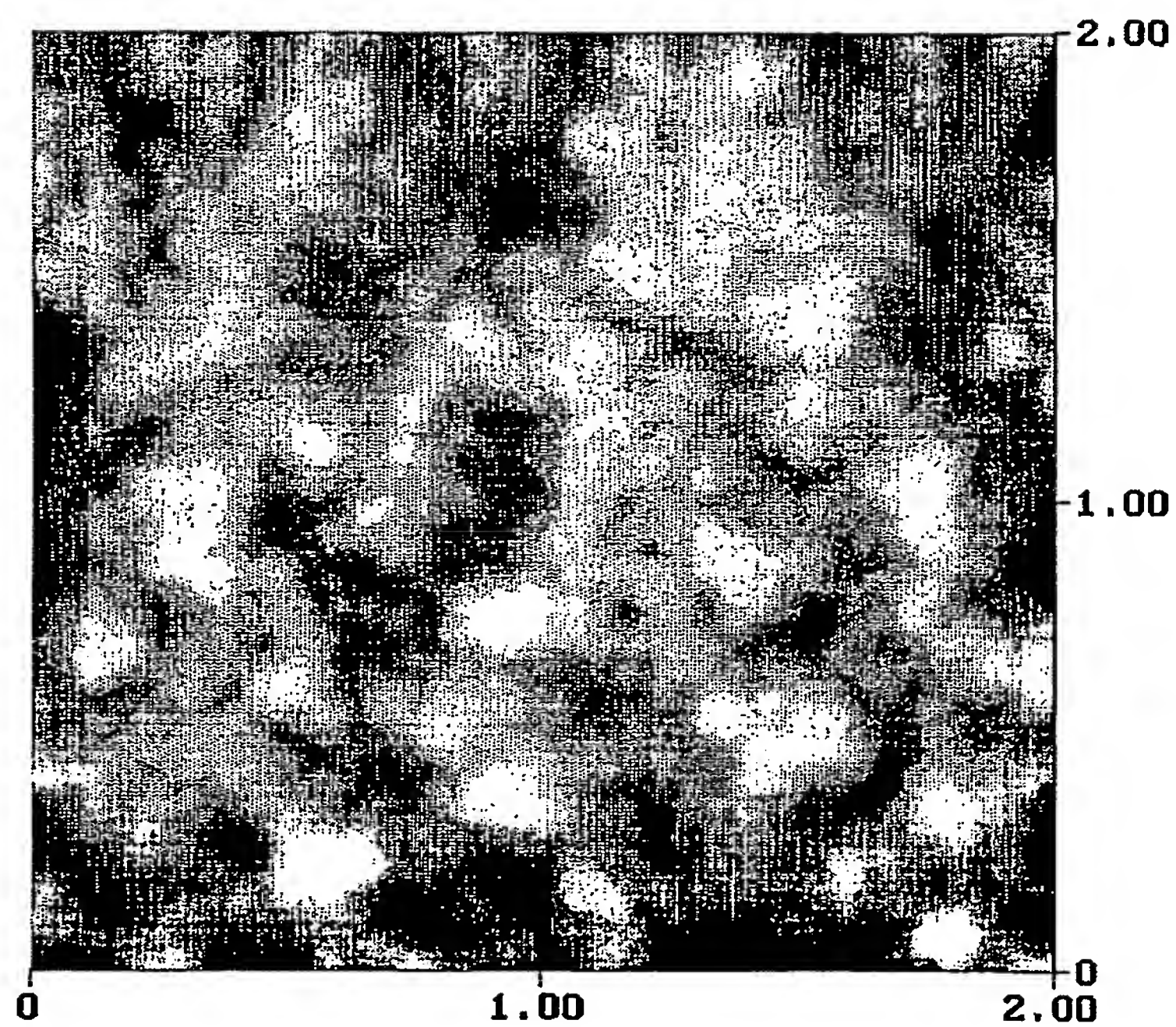


FIG. 9

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